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Quarterly Progress Report

Division 8

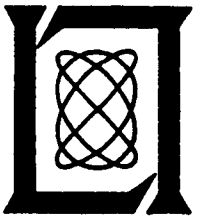
Solid State

15 January 1963

Lincoln Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Lexington, Massachusetts



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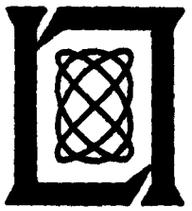

INTRODUCTION

This abbreviated report covers the work of Division 8 from 1 October through 31 December 1962. A more detailed presentation is covered by the Solid State Research report for the same period.

Benjamin Lax
Head, Division 8

James W. Meyer
Associate Head

Alan L. McWhorter
Assistant Head

15 January 1963

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REPORTS BY AUTHORS IN DIVISION 8

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1855	The Effect of Ion Mass and Ion Energy on the Sensitivity of Ilford Q_2 Plates as Ion Detectors in Mass Spectrography	E.B. Owens	Appl. Spectroscopy 16, 148 (1962)
1922	Theory of Galvano-Thermomagnetic Energy Conversion Devices. I. Generators	T.C. Harman J.M. Honig	J. Appl. Phys. 33, 3178 (1962)
1933	Elastic Strain Energy Associated with the "A" Surfaces of the III-V Compounds	R.E. Hanneman M.C. Finn H.C. Gatos	J. Phys. Chem. Solids 23, 1553 (1962)
1935	New Method for Calculating Molecular Orbitals with Application to Cyclic Systems	L. Eyges	Phys. Rev. 128, 1715 (1962)
1945	Theory of Galvano-Thermomagnetic Energy Conversion Devices. II. Refrigerators and Heat Pumps	T.C. Harman J.M. Honig	J. Appl. Phys. 33, 3188 (1962)
1951	High Pressure Phase Transition in Mercury Selenide	J.A. Kafalas H.C. Gatos M.C. Lavine M.D. Banus	J. Phys. Chem. Solids 23, 1541 (1962)
1965	The Relation Between the Chemical Potential of Electrons and Energy Parameters of the Band Theory as Applied to Semiconductors	W.W. Harvey	J. Phys. Chem. Solids 23, 1545 (1962)
1981	The Madistor – A Magnetically Controlled Semiconductor Plasma Device	I. Melngailis R.H. Rediker	Proc. IRE 50, 2428 (1962)
1991	Operating Characteristics of Transverse (Nernst) Anisotropic Galvano-Thermomagnetic Generators	T.C. Harman J.M. Honig	Appl. Phys. Letters 1, 31 (1962)

* Reprints available.

PUBLISHED REPORTS (Continued)

Journal Articles (Continued)

JA No.			
2005	High Field Superconductivity in Niobium	S. H. Autler E. S. Rosenblum K. H. Gooen*	Phys. Rev. Letters 9, 489 (1962)
2032-I	Theory of Semiconductor Maser of GaAs	A. L. McWhorter H. J. Zeiger B. Lax	J. Appl. Phys. 34, 235 (1963)
2032-II	Semiconductor Maser of GaAs	T. M. Quist R. H. Rediker R. J. Keyes W. E. Krag B. Lax A. L. McWhorter H. J. Zeiger	Appl. Phys. Letters 1, 91 (1962)
2037	Oscillatory Quantum Effects in the Ultrasonic Velocity in Bismuth	J. G. Mavroides B. Lax K. J. Button Y. Shapira*	Phys. Rev. Letters 9, 451 (1962)
2043	High Speed Heterojunction Photodiodes and Beam-of-Light Transistors	R. H. Rediker T. M. Quist B. Lax	Proc. IEEE 51, 218 (1963)
2056	Growing Helical Density Waves in Semiconductor Plasmas	C. E. Hurwitz A. L. McWhorter	Phys. Rev. Letters 10, 20 (1963)
MS-628	Antiferromagnetic Materials and Their Application at Millimeter and Submillimeter Wavelengths	G. S. Heller	NEREM Record, Session 4 (1962)

UNPUBLISHED REPORTS

Journal Articles

JA No.			
1995	Operating Characteristics of Nernst Refrigerators for Anisotropic Materials	T. C. Harman J. M. Honig	Accepted by Appl. Phys. Letters
2001	Magneto-Reflection in Bismuth	R. N. Brown J. G. Mavroides B. Lax	Accepted by Phys. Rev.

* Author not at Lincoln Laboratory.

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Journal Articles (Continued)

JA No.			
2028	Injection Electroluminescence in Gallium Antimonide	A. R. Calawa	Accepted by J. Appl. Phys.
2040	High Field Antiferromagnetic Resonance in CR_2O_3	S. Foner	Accepted by Phys. Rev.
2045	High Pressure Tetragonal Phase of InSb	M. D. Banus R. E. Hanneman A. N. Mariano E. P. Warekois H. C. Gatos J. A. Kafalas	Accepted by Appl. Phys. Letters
MS-679	Antiferromagnetic Properties of $NiTiO_3$	G. S. Heller J. J. Stickler S. Kern A. Wold*	Accepted by J. Appl. Phys.
MS-752	Comments on the Lincoln Laboratory GaAs Diode Maser	R. H. Rediker	Accepted by Proc. Symposium on Lasers and Applications, Ohio State University, 7-8 November 1962

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596	The Anodic Dissolution Reaction at Semiconductor Electrodes	W. W. Harvey	Phenomena at Interfaces Symposium, The Electrochemical Society, Boston, 19 September 1962
619A	Nonlinear Effects at Optical Frequencies	D. F. Edwards J. G. Mavroides B. Lax	Seminar on Nonlinear Optics, Burroughs Corporation, Paoli, Pennsylvania, 18 October 1962
636	Heating with Atoms, Electrons, and Photons – A Survey of the Heat Transfer Spectrum	T. B. Reed	American Society of Metals, New York, 23 October 1962
647B	Recent Work on Magneto-Plasma and Injection-Luminescent Semiconductor Devices	R. H. Rediker	IRE, PGED, Pittsburgh, 18 October 1962
657A	Magneto-Optical Effects in Metals and Graphite	M. S. Dresselhaus	Solid State Physics Seminar, Cornell University, 15 November 1962

* Division 5.

† Titles of Meeting Speeches are listed for information only. No copies are available for distribution.

Meeting Speeches (Continued)

MS No.			
674A	Raman Maser and Spectroscopy	H.J. Zeiger P.E. Tannenwald	Solid State Physics and Metallurgy Colloquium, Harvard University, 30 October 1962
681	High Efficiency Injection Electroluminescence in GaAs	T.M. Quist R.J. Keyes	IRE, PGED, Washington, 25-27 October 1962
695	Radiation Emitted by GaAs Diodes	T.M. Quist R.J. Keyes	IRE, PGMTT, M.I.T., 28 November 1962
698	Operating Characteristics of Galvano-Thermomagnetic Generators and Refrigerators for Anisotropic Materials	T.C. Harman J.M. Honig B.M. Tarmy	American Physical Society, Cleveland, 23-24 November 1962
700	Mass Spectroscopy in Solids	E.B. Owens	Southwest Regional Meeting, American Chemical Society, Dallas, 6 December 1962
711	Recombination Radiation Emitted by Gallium Arsenide	R.J. Keyes T.M. Quist	Symposium on Lasers and Applications, Ohio State University, 7-8 November 1962
717	g-Factors in Semiconductors	L.M. Roth	Physics Colloquium, Tufts University, 16 October 1962
729	High Magnetic Field Research	B. Lax	IRE, Los Alamos, 2 November 1962
743	Antiferromagnetic Resonance in the Ilmenites	G.S. Heller	Seminar, M.I.T., 2 November 1962
744	Ferro- and Antiferromagnetism in a Simple Cubic Lattice	G.F. Dresselhaus	Solid State Physics Seminar, Cornell University, 15 November 1962; Lecture, Ford Motor Company, Dearborn, Michigan, 7 December 1962
759	Discussion of paper "Correlation of Factors Influencing the Pressures Generated in Multi-Anvil Devices"	M.D. Banus	Symposium on High Pressure Measurements, ASME, New York, 27-30 November 1962
760	Recent Millimeter Wave Experiments in Solids	G.S. Heller	Physics Colloquium, Northeastern University, 18 December 1962; Millimeter and Submillimeter Conference, IRE, Orlando, Florida, 8-10 January 1962

* Author not at Lincoln Laboratory.

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765	A Cluster Calculation of Magnetic Properties	G.F. Dresselhaus	Physics Department Colloquium, Northwestern University, 5 December 1962
766	Chemistry and Physics of HgTe, HgSe, and Their Alloys	A.J. Strauss	Seminar, Xerox Corporation, Rochester, New York, 12 December 1962
773	GaAs Diode Maser	H.J. Zeiger	Seminar on Masers, M.I.T., 17 December 1962; Physics Seminar, M.I.T., 11 January 1963

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I. SOLID STATE DEVICE DESIGN

A pulsed magnetic field apparatus is being built to study magneto-optical effects in semiconductors. Preliminary experiments in fields of 250 kilogauss have not shown the shift in the wavelength of the narrow-line incoherent radiation from GaAs diodes that would be expected if either the 0.07-m_o electron or the 0.12-m_o light hole were involved in the transition producing this radiation.

GaAs alloy diodes have been fabricated by evaporating known thicknesses of Au and Zn on n-GaAs and then alloying these films at 550°C for less than 5 seconds to produce rectifying contacts. While the magnitude of the forward current of these diodes can be explained in terms of a metal-semiconductor (Schottky) barrier, this model has not been able to account for the increasing values of n in the $I = I_o \exp[qV/nkT]$ relationship as the film thickness is decreased. While for a 5000 Å film n = 1.1, for a 300 Å film n = 1.5.

GaAs diode masers have been fabricated and the spectrum and intensity of the emitted coherent light studied as a function of the amplitude and width of the diode current pulses. For typical diode masers the emitted radiation varied linearly with current density up to a threshold of about 10^4 Åcm^{-2} at 77°K or about 700 Åcm^{-2} at 4.2°K, above which the intensity of the radiation increased radically. Well above this threshold for coherent light emission, the light output again became linear with current and absolute measurements indicate the diode maser is operating at nearly unity quantum efficiency. Thus, for the maximum current of 190 amperes through a diode of junction area 7×10^{-3} cm^2, 280 watts have been radiated (for 5 μsec) from an area estimated to be less than 10^{-4} cm^2. At 4.2°K the linewidth of the emitted coherent radiation from a more recent diode has been measured to be less than 0.25 Å. While in the laser mode, the narrow-line emission increased with current pulse amplitude; as the pulse length was increased, other emission lines appeared for several diodes and grew continuously in intensity, even reaching a higher intensity than the original emission line. These other lines, which were still narrow and represent laser modes, were believed to be associated with sample heating. Techniques are being developed to protect the surfaces of the reflecting ends of the semiconductor maser. The threshold current of a given diode has in several cases been increased by temperature cycling in which a film has been produced on these ends. These threshold currents can be subsequently reduced to close to their initial values by swabbing the reflecting sides with acetone.

Audio and video signals have been successfully transmitted from the top of Mt. Wachusetts to Lincoln Laboratory, a distance of 30 nautical miles, via the infrared radiation emitted by a GaAs diode. The experiment was performed at night at a time when the atmospheric attenuation of the radiation over the path was about 5 db. The audio signals at the receiver were orders of magnitude above the signal noise; the television signals, under best operating conditions, were a factor of 20 greater than noise. Further improvement in performance can be expected from improved system design. It should be borne in mind, however, that the operation of infrared communication links will be markedly affected by atmospheric visibility.

An idealized electromagnetic model of the GaAs diode maser has been considered. On the basis of this model, an expression for the threshold condition for onset of oscillations has been obtained. A theoretical estimate of the angular spread of the beam has been made, and is found to be reasonably consistent with observation.

A GaAs-Ge heterojunction diode has been proposed as a high-speed photodetector for the radiation emitted from either a coherent or incoherent GaAs diode infrared source. The very-high-frequency response of the heterojunction diode is possible because of the considerably different absorption of the incident radiation in Ge and GaAs. The GaAs side is illuminated, but less than 0.01 percent of the radiation is absorbed in a distance of 10 microns, while over 90 percent of the radiation will be absorbed in the Ge within 1 micron of the junction. Thus, appropriately chosen p-n heterojunctions can insure that the radiation is absorbed close to the junction and that the transit time of the photoproduced carriers is consistent with high-frequency photodiode operation.

It should also be possible to fabricate a transistor with an infrared-emitting GaAs p-n junction as emitter and an n-GaAs, p-Ge heterojunction as collector. This beam-of-light transistor has several advantages over conventional transistors: (1) Very low lifetime material can be used; thus the transistor field is opened up to a host of different materials. (2) Carrier injection need not be from emitter to base; thus the base resistance can be significantly reduced with no concomitant increase in emitter transition layer capacitance or emitter series resistance. (3) The transport from emitter to collector is at the speed of light in the material. In order to collect a large percentage of the emitted radiation at the collector, the transistor surfaces should be coated with reflecting coatings and the transistor geometry should be such as to reflect the infrared toward the collector. If the infrared-emitting diode is operated as a maser, it may be possible, with an appropriately placed collector, to have a grounded-base current gain extremely close to unity.

The electrical parameters expected from a specific design of a beam-of-light transistor have been compared with those of a mesa transistor, which represents the current state of the art in making high-frequency transistors. Both incoherent-mode infrared emission and coherent-mode infrared emission have been considered. The proposed structure is shown to have slightly greater speed in common emitter configuration [f_T of 4.5 Gcps (coherent) and 4.1 Gcps (incoherent) vs 3.6 Gcps], and a much higher gain factor at 1 Gcps in common base configuration [1400 (coherent) and 800 (incoherent) vs 25]. Also, since the base layer of the proposed structure is much wider than that of the mesa transistor (10 microns vs 0.25 micron), and since its speed is relatively independent of the base width, it should be much easier to fabricate than the corresponding mesa transistor.

An open-tube method, in which $H_2 + AsCl_3$ is used to transport Ga from a bath of molten metal, has been used to produce mirror-finish GaAs epitaxial layers. Diodes have been fabricated by depositing n-type undoped epitaxial layers on p-type substrate. These diodes are now being evaluated for injection electroluminescence.

Initial machine computation of the rate of cascade capture by ionized impurities, using an improved version of M. Lax's "giant trap" theory, has given results significantly larger than Lax's. This is to be expected, since the present theory permits capture by more highly excited states.

II. CHEMISTRY

For predominantly covalent electronic semiconductors, the thermodynamic activity of holes has been shown to contain the thermodynamic activity of the semiconductor species (approximately given by its mole fraction). Thus, for example, by formulating the intrinsic ionization equilibrium alternatively as a transition of electrons between valence and conduction bands and as a self-ionization of the semiconductor species, the activity a_p of holes is found to vary inversely as a_{GaAs}, a_{Si}^2, etc.

The electric field due to diffusion of carriers away from the interface has been used to detect carrier generation by electrochemical reaction. The reaction of n- and p-type germanium with alkaline ferricyanide or 8N nitric acid was attended by generation of excess carriers; this effect was not observed in the reaction of InSb with bromine-methanol or nitric acid-lactic acid etchants.

The dependence of measured values of Seebeck coefficient α and electrical resistance R of PrO_x on temperature and composition has been compared with theoretical predictions for electron-transfer semiconductors. For compacted samples in the range of compositions investigated ($1.59 \leqslant x \leqslant 1.81$), α is approximately independent of temperature and, moreover, exhibits essentially the predicted dependence upon x. The composition dependence of R, measured at two fixed temperatures, is also compatible with theory.

Measured electrical properties of single-crystal samples in the composition range $1.50 \leqslant x \leqslant 1.53$ support the conclusion that an electron-transfer model pertains to semiconducting, nonstoichiometric PrO_x. Furthermore, the large changes in α, and in resistivity and its temperature dependence observed for the nearly stoichiometric sesquioxide, indicate the existence of a secondary conduction mechanism, which is overshadowed by the primary mechanism for $x > 1.5$.

Two types of hanging mercury drop electrode are being investigated with a view to realizing increased sensitivity over conventional polarography. Greater precision has resulted from using the Shain electrode (mercury suspended from a previously amalgamated platinum wire) than from using the Kemula electrode (mercury suspended from the tip of a mercury-filled capillary).

A method has been developed for the analysis of indium telluride, which is sensitive to about one part per thousand. Indium is determined by direct titration with EDTA at pH 2.4 to a potentiometric endpoint using a gold amalgam electrode; tellurium is determined by adding excess $K_2Cr_2O_7$ and back-titrating with $Fe(NH_4)_2(SO_4)_2$.

III. MATERIALS RESEARCH

The partial pressures of Te_2 and SnTe molecules in equilibrium with SnTe have been measured by means of an optical absorption technique used previously. The Te_2 pressure depends strongly on the composition of the solid SnTe, while the pressures of SnTe in equilibrium with Sn-saturated and Te-saturated compounds are found to be the same within the limits of experimental error. A value of 51 kcal/mol is obtained for the heat of sublimation of SnTe.

The spectra of induction plasmas generated at pressures between 10 μ Hg and 1 atmosphere have been recorded with a grating spectrograph. Plasmas operating in the high-power mode at

pressures up to 100 mm Hg and Geisler tubes operating at pressures of only a few millimeters of mercury are found to have spectra which are similar in both line intensity and linewidth.

The structures of high-pressure phases of semiconducting compounds are being determined by x-ray diffraction measurements made at high pressures with a diamond-cell transmission camera. Both CdS and CdSe transform from wurtzite to sodium-chloride structure, while HgTe transforms from zincblende to cinnabar (HgS) structure. Data for the high-pressure forms of CdTe and SnTe are being analyzed. The high-pressure cubic phase of InTe obtained by direct synthesis at high temperature and pressure has also been prepared by transforming the tetragonal phase synthesized at atmospheric pressure.

IV. BAND STRUCTURE AND SPECTROSCOPY OF SOLIDS

The galvano-thermomagnetic effects in semimetals and semiconductors are being studied extensively both from a theoretical and an experimental viewpoint. Expressions for the six basic galvano-thermomagnetic transport coefficients have been put into a closed analytic form for the following special cases: the extreme limits of classical or degenerate statistics, weak or strong magnetic field limits, and for parabolic and nonparabolic bands. The variation of the components of the general Nernst and Seebeck tensors of bismuth has been measured with magnetic fields up to 50 kilogauss. Oscillations periodic in 1/H have been seen in the 30- to 50-kilogauss region. The large observed values of the Nernst coefficient suggest that a multiband model is required to explain the phenomenon. The analysis of the transverse anisotropic galvano-thermomagnetic refrigerator is being continued. Much of this work has been submitted for publication.

Magnetoreflection effects which have been seen previously in semiconductors and semimetals have now been observed in a metal, silver. Preliminary measurements have been made on a single crystal of silver in the ultraviolet at low temperatures. An analysis of the observed magnetic field effects is now in progress.

Oscillations of the de Haas-van Alphen type, previously observed in the attenuation of sound in bismuth, have been shown to be present in the velocity of sound also. The values of the effective masses in bismuth found from the velocity variations are in agreement with those previously found by other methods. The small values of the amplitude of the oscillations indicate that a two-carrier or many-valley model of bismuth will be required to explain the effect. Details of the results have been published.

Recent experimental results indicate that the Raman spin lattice relaxation rate of donors in silicon, previously studied theoretically, does not have the proper temperature dependence and is too small by a factor of 10^4. Various mechanisms which give the proper T^9 temperature dependence, all of which involve interband effects, have been investigated.

The formulas recently developed for the exchange energy of electrons in a periodic lattice have been applied to the case of s-like bands. It is found that the effect of the periodic lattice on dE/dk at $k = k_o$ is too small to be experimentally observable. The total exchange energy for sodium has been evaluated and found to be in agreement with previous calculations. This work is being prepared for publication.

V. SPECTROSCOPY OF MAGNETIC SOLIDS

Antiferromagnetic resonance studies of powdered $CoTiO_3$ and $FeTiO_3$ are under way, at frequencies from about 35 to 140 kMcps. Preliminary observations of antiferromagnetic resonance as a function of temperature have been made.

Paramagnetic resonance of NiF_2 above the Néel temperature has been observed. Thus far, no reasonable fit to a single-ion spin Hamiltonian can be made. Measurements of linewidth in antiferromagnetic resonance of MnF_2 single crystals and powders have been made, from low temperatures to the Néel temperature.

Experiments to measure second-order exchange interactions by the spin wave resonance method have been resumed. The aim is to verify the $T^{5/2}$ temperature variation of the exchange constant.

The study of Raman emission from a number of crystals excited by an intense ruby laser pulse has been continued. Particular emphasis has been placed on the excitation of vibrational Raman lines in solids in view of the fact that coherent Raman radiation from organic liquids has been reported.

The current-carrying properties of superconducting Nb in a magnetic field are being studied as a function of temperature. In some cases, the resistance of niobium can decrease by orders of magnitude as the magnetic field or temperature is raised. Evidence is accumulating that these surprising phenomena are related to the Abrikosov negative-surface-energy model of superconductors.

Studies of the spin Hamiltonian for Fe^{3+} in Al_2SiO_5 and Cr^{3+} in SnO_2 are being made by electron spin resonance in the frequency range from about 24 to 140 kMcps. Tabulation of rotation matrices for standard crystalline fields to order 6 has been completed.